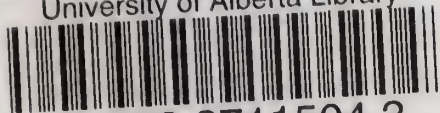


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The direct oxidation of natural  
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THE DIRECT OXIDATION OF NATURAL GAS  
AT HIGH PRESSURE.

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by  
J.W. Broughton, B.Sc.,  
University of Alberta.

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A THESIS

presented in partial fulfilment of the  
requirements for the degree  
of MASTER OF SCIENCE.

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## INTRODUCTION.

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Of the few general reactions of hydrocarbons, oxidation is one of the most common and certainly, from the practical point of view, the most important. It may be brought about by various means such as the use of temperatures, pressure and catalysts of various kinds. Because it is a general reaction and allows the investigation of many characteristics of hydrocarbons, it has been the subject of much study. These studies of oxidation of hydrocarbons are of importance from many obvious theoretical points of view regarding equilibrium, catalysis, and mechanism of reaction, and bear upon such practical problems as the combustion of fuels and the utilization of the enormous supplies of hydrocarbons available.

The significance of the work in general may be emphasized by the fact that the estimated quantity of methane alone available in 1929 was  $2 \times 10^{12}$  cu. feet (11). The particular significance of the work here lies in the large supplies in the Province of Alberta of natural gas whose principal constituent is methane. The available daily production in this





province under wide open conditions in the proven fields might reach 750,000,000 cu. ft. By fractionation the individual paraffin hydrocarbons could be separated at low cost if necessary and offer a source of raw material that should stimulate investigations leading to commercial utilization.

That the work is of great theoretical interest is made obvious by the large amount of published results reviewed briefly in the following section dealing with the mechanism and control of oxidation of hydrocarbons. The published work has been concerned with, first, the production of useful oxygenated organic compounds, such as the alcohols and aldehydes, with as little as possible oxidation to oxides of carbon and water, and secondly, with the elucidation of the mechanism of oxidation with particular reference to the combustion of hydrocarbons as fuels in internal combustion engines.

The present work to be described is concerned chiefly with the first of the above and more particularly with the production of methyl alcohol, formaldehyde or formic acid, and any additions to knowledge of the processes of oxidation are secondary. The production of alcohols or even aldehydes and acids by





direct oxidation of the appropriate hydrocarbons is a process offering obvious attractions. At present two or more stages are necessary for the conversion of hydrocarbons to alcohols which involve either conversion to water gas, followed by higher pressure syntheses, or halogenation followed by hydrolysis. The direct oxidation is a simpler process in theory and, if practical, would offer a much superior and economical process for the production of alcohols and related compounds.

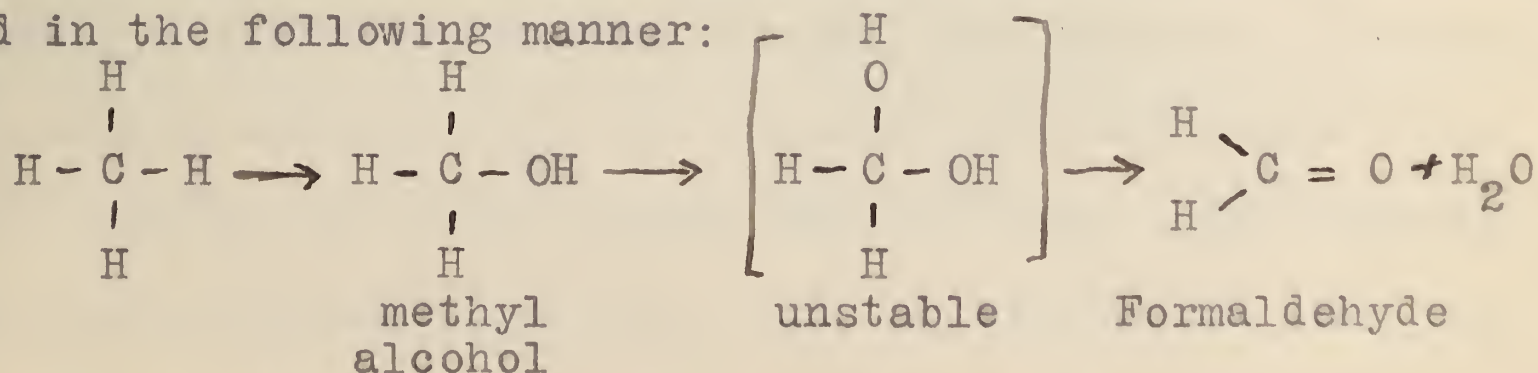
As an addition to the knowledge of the subject and in the hope of obtaining results of practical value, the direct oxidation of a high methane natural gas has been examined over a variety of catalysts and at pressures to the neighborhood of 200 atmospheres at various rates of flow and temperatures.



## Literature Review.

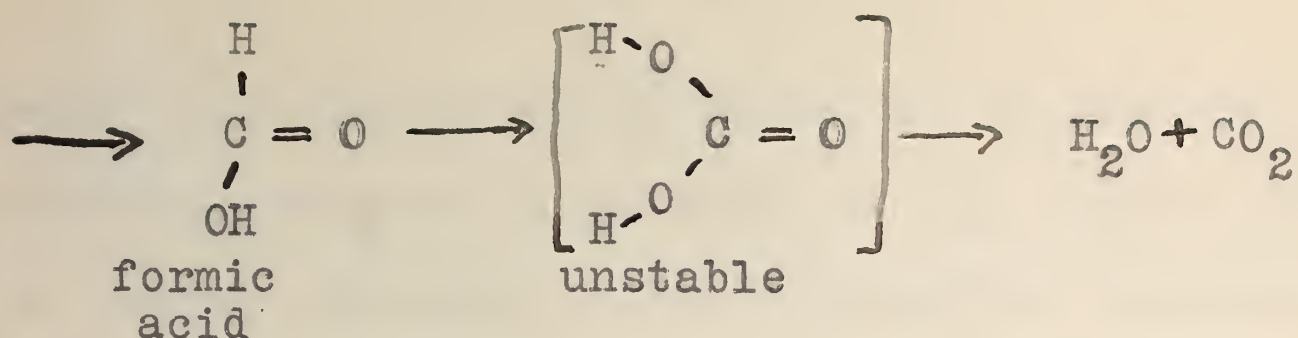
The systematic investigation of the mechanism of combustion of hydrocarbons has received much attention. That the course of the reaction is complex there is no doubt, and the importance of isolating and identifying the intermediate products cannot be over emphasized from both the practical and theoretical viewpoints.

The most important and comprehensive work was initiated by Bone with various collaborators about 1900. As a result of Bone's early investigation (4) the "hydroxylation" theory was proposed and since that time this theory has served as a guiding principle in all his work to date. Most of this work has been carried out with the simple hydrocarbons as methane and ethane and, at least for these substances, the hydroxylation theory has been well established at low and high pressures. The theory postulates essentially the formation of successive hydroxylated compounds as may be illustrated in the following manner:

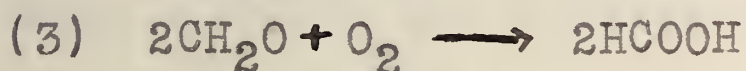
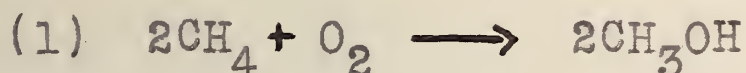








On writing the above reaction stoichiometrically it is seen that methyl alcohol and formic acid are formed with a contraction in volume, whereas formaldehyde involves an expansion:



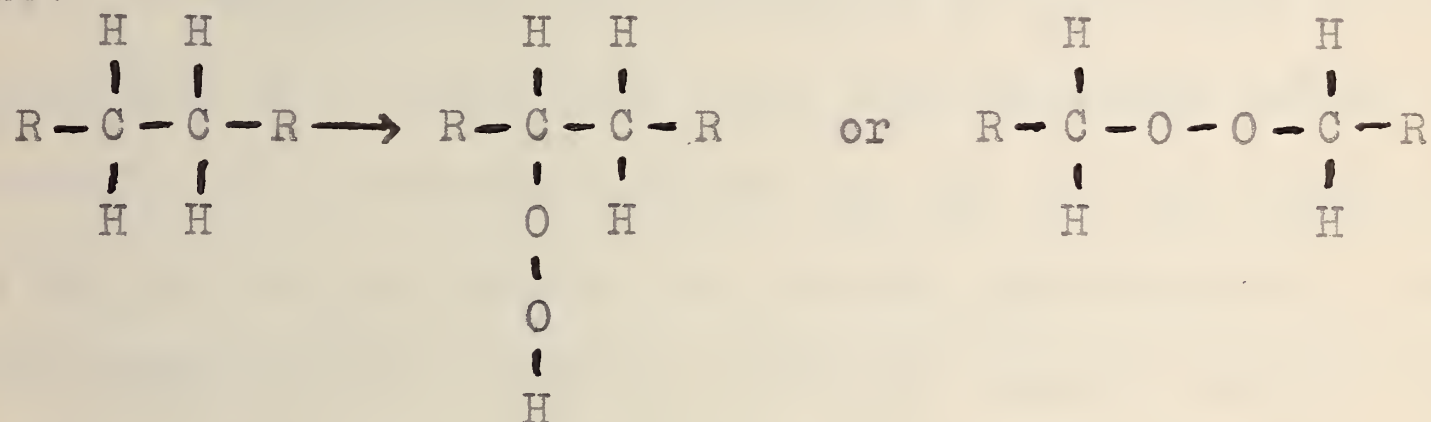
Hence the effect of increasing the pressure in the reacting system would be to favor the survival of methyl alcohol and formic acid at the expense of the formaldehyde.

The hydroxylation theory has not been generally accepted until recently except for the simpler hydrocarbons. An alternative theory, the "peroxide" theory has received considerable support in the past and, while hardly acceptable for the simpler hydrocarbons at present, it serves equally well and has experimental support for the combustion of the higher hydrocarbons. Callendar(8) and, more recently Dumanois (10), in connection with the combustion of gasoline hydrocarbons subscribe to the theory.





Briefly this theory may be described as postulating the initial formation of a peroxide by the direct addition of an oxygen molecule to the hydrocarbon molecule which is followed by decomposition to an aldehyde and water, thus:



Edgar (18) in his studies of the oxidation of the octanes and similar hydrocarbons cannot subscribe to either theory, in that, among other reasons he finds the evidence for peroxide formation doubtful and none at all for alcohol formation. At least for these higher hydrocarbons, Edgar proposes and presents evidence for the belief that oxidation to an aldehyde and water is the primary step. Each succeeding step consists of the oxidation of the aldehyde to the next lower aldehyde with the formation of  $\text{CO}_2$ .

Thompson and Hinshelwood (23) suggest that while "the first stage of the reaction is the formation of an unstable peroxide ..... there is no doubt that Bone's interpretation of the complete course of oxida-



tion as a process of successive hydroxylation is essentially correct," and that "the two views are not incompatible, and a combination of them suggests an explanation of the facts."

Evidence of the formation of peroxides is very meagre and in no case have they been detected before the formation of aldehydes towards the end of the induction period, or in the case of the simple hydrocarbons. For these reasons, <sup>and</sup> also because aldehydes fairly readily form peroxides, Bone is rigidly opposed to the theory that peroxides are formed as an initial step in the combustion of hydrocarbons, at least with respect to the lower members of the series. In the present work where only the simple hydrocarbons are used, the hydroxylation theory will be accepted as a working hypothesis sufficient to clarify all the observed facts.

The first evidence of the validity of the hydroxylation theory was obtained by Bone and Wheeler (7) who showed that when methane-oxygen mixtures were circulated through a reaction tube containing fragments of porous porcelain maintained at a temperature between  $450^{\circ}$  and  $500^{\circ}\text{C}$ . formaldehyde was formed to the extent of 13% to 20% of the methane burnt. Small amounts of





formic acid were also detected. However, any direct evidence of the formation of methyl alcohol as an intermediate product was entirely wanting. The slow combustion of ethane with oxygen at atmospheric pressure yielded similar results, acetaldehyde, formaldehyde and formic acid being identified among the products of reaction, but not ethyl alcohol nor methyl alcohol.

As a result of much research at atmospheric pressure it has been shown conclusively by Bone and his collaborators (4), Wheeler and Blair (24), Medvedev (15), and Berl and Fischer (2), that oxygenated derivatives could be formed by the partial oxidation of gaseous hydrocarbons, although only traces of alcohols and acids were obtained. However, yields of aldehydes were too small to warrant the application of these processes to industrial operation.

More recently C.H. Bibb (3) investigated the effect of nitrogen peroxide as a catalyst in the partial oxidation of hydrocarbons at atmospheric pressure. Air containing nitrogen peroxide was mixed with natural gas or with propane and passed through a heated chromenichel steel tube. Yields of formaldehyde as high as 19.1 lbs. of 40% formalin per 1000 cu.ft. of natural gas were obtained at  $735^{\circ}\text{C}$ . at the appropriate rate of flow. The partial oxidation of propane by air with





nitrogen peroxide as a catalyst showed yields of 19.8 lbs. of 40% formalin solution per 1000 cu. ft. of gas under similar conditions.

The use of a large apparatus and recirculating the gaseous products, after removing the formaldehyde with water, resulted in yields of 26.5 lbs. of 40% formalin per 1000 cu.ft. of gas.

The method is not commercially very practicable as the formalin solutions contained nitric acid in proportion up to as much as 33% of the formaldehyde which gradually oxidized the formaldehyde to formic acid.

The catalytic partial oxidation of various mixtures of methane, ethane and natural gas with oxygen have also been studied by Layng and So<sup>u</sup>rkup (13) using the dynamic method at atmospheric pressure within the temperature range of 100° to 700°C.

For the production of alcoholic and aldehydic intermediates copper and silver, and oxides of these metals, activated charcoal, platinum oxide and barium peroxide proved to be unsatisfactory catalysts on the basis of hydrocarbon consumed and products obtained.

Small amounts of nitrogen peroxide when added to hydrocarbon-oxygen mixtures and passed through heated capillary tubes, were found to promote the oxidation





materially, yields of oxygenated derivatives varying from 15% to 30% of the amount of hydrocarbon oxidized being obtained.

Auxiliary solid catalysts used in conjunction with nitrogen peroxide activated the decomposition of intermediate products without materially increasing the amount of hydrocarbon decomposed. Methyl nitrite was also shown to have a promoting action on the partial oxidation reactions of hydrocarbons.

Substantial proof of the production of alcohols as an intermediate product was not obtained until the partial oxidation of hydrocarbons was carried out at high pressures.

Newitt and Haffner (17) using a static method investigated the oxidation of methane at pressures of 49, 106 and 150 atmospheres in a 500 ccm. capacity reactor from 335°C. to 393°C. They were able to isolate sufficient quantities of methyl alcohol to form the p-nitrobenzoic acid methyl ester which was identified by its melting point. The reactions were followed by the changes in pressure and temperature that occurred with time from the moment of inlet of the gas mixture until the reaction was stopped by expanding the reacting mixture rapidly into a collect-





ting vessel. Catalysts as such were not used but it is probable that the steel walls of the container exerted some catalytic effect. A mixture of pure methane with oxygen in the ratio of 8.1:1 was used in all their experiments.

It was found that at each pressure there was a definite temperature at which maximum survivals of alcohol and aldehyde were obtained. This was not the lowest temperature at which reaction would take place, but usually one giving a medium time of reaction.

The effect of increasing the pressure was not only to increase the amounts of both methyl alcohol and formaldehyde surviving, but also to increase the ratio  $\text{CH}_3\text{OH}/\text{HCHO}$ .

Formic acid was obtained in quantities too small to be determined with accuracy. The authors record optimum conditions of 106.4 atmospheres at  $341^\circ\text{C}$ . for 12 minutes giving a yield of 22.3% of the methane burnt as methyl alcohol and 0.75% as formaldehyde. Maximum yields of formaldehyde occurred at shorter times of between 1% and 2% of the methane burnt. The high yield of methyl alcohol is particularly noteworthy when it is realized that little or no methyl alcohol has been obtained by oxidation at atmospheric





pressure. The formaldehyde yield is low compared to the reported values of around 10% in atmospheric pressure experiments as might be predicted as a consequence of applying high pressures.

The work of Newitt and Haffner was preceded by that of Yoshikama (25) who investigated the partial oxidation of methane at high pressure by the static method and with about the same results. Yoshikama's publication, however, is not readily obtainable.

The literature available does not record any investigations dealing with the oxidation of methane under pressure in the presence of catalysts.



## EXPERIMENTAL METHODS.

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### Materials.

Natural gas from the Viking field was used in all experiments. This gas is composed mainly of methane as shown by the following distillation analysis<sup>1</sup>:

Methane	95.7 %
Ethane	1.4
Propane	0.9
Nitrogen	2.0

Since the gas is being odorized by the introduction of alkyl disulfides and mercaptans to obviate fire hazards in the City of Edmonton it was necessary to purify it before use. The method of purification is described in a later section.

The oxygen used in making up oxygen gas mixtures was the commercial material obtained from liquid air and compressed in cylinders.

Mixtures of natural gas with oxygen were made by simultaneously metering the two gases in the proportion desired into a water-sealed gas holder of twenty cubic feet capacity. By this procedure it was not necessary to wait for mixing of the gases by diffusion.

The mixture was dried over calcium chloride before com-

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1. Obtained through the courtesy of the mines branch.





pressing and stored with the equipment shown in Figure 1. The oxygen content of the resulting mixtures varied slightly with different lots between 7.3% and 7.5%. Higher oxygen concentrations were not considered safe as the explosive range increases in width with pressure to about 10% oxygen at 200 atmospheres.

Most of the catalysts investigated were oxides of metals having more than one possible valence. These oxides were known to be good oxidation catalysts, which property is probably due to their power of acting as oxygen carries. The catalysts prepared and used in the experiments included barium peroxide, vanadium pentoxide, blue tungsten oxide, Hopcalite I, Hopcalite II and silver precipitated on asbestos.

Two samples of barium peroxide were prepared by decomposition of barium nitrate as described by Mellor (26). On heating barium nitrate above its melting point decomposition takes place with the evolution of oxides of nitrogen, the residue consisting mainly of a mixture of barium oxide and barium peroxide. The first barium peroxide catalyst prepared in this manner was fairly porous and was used without further treatment in the first four experiments. The second barium peroxide catalyst was made in a somewhat different manner. Pumice stone of about 5 mesh size was saturated with





barium nitrate solution, dried, and ignited to give the oxide and peroxide. The catalyst was converted as completely as possible to the peroxide by heating in the autoclave to  $450^{\circ}\text{C}$ . with oxygen at a pressure of 1000 lbs. per sq.in.

Vanadium pentoxide supported on asbestos was made by boiling long-fiber asbestos in a saturated solution of ammonium metavanadate, drying and heating until the ammonia was completely expelled.

Blue tungsten oxide was prepared by reduction of tungstic oxide on asbestos by hydrogen at a dull red heat. Asbestos saturated with ammonium metatungstate solution was dried and heated to give tungstic oxide which was subsequently reduced.

The Hopcalite catalysts were prepared according to the methods of Merrill and Scalione (14). The first and more active catalyst known as Hopcalite I consists of a mixture containing 50% of  $\text{MnO}_2$  and 30%  $\text{CuO}$  promoted by 15%  $\text{Co}_2\text{O}_3$  and 5%  $\text{Ag}_2\text{O}$ . The other catalyst, Hopcalite II, of lesser activity, consists of a mixture containing 60%  $\text{MnO}_2$  and 40%  $\text{CuO}$ . The activity of these catalysts depends upon the method of preparation of the oxides and their purity. The oxides were prepared by separate precipitation from aqueous solution followed by very complete washing to remove





soluble electrolytes. The oxides were mixed wet, kneaded thoroughly and dried gently at 50°C. The cake obtained was then crushed, screened and dried at 200°C. before use. Manganese dioxide was prepared by oxidation of manganous sulfate in 77% sulfuric acid solution by potassium permanganate according to Fremy's method. Copper oxide was prepared by precipitation with sodium hydroxide from hot copper sulfate solution, and silver oxide from silver nitrate solution with sodium hydroxide solution. Cobaltic oxide was prepared by precipitation of cobaltous hydroxide from cobaltous sulfate solution by sodium hydroxide, followed by oxidation to cobaltic oxide with NaOCl. In the case of Hopcalite I, the silver oxide was formed in a suspension of the other three oxides which had been prepared individually. In the case of Hopcalite II, the copper oxide was formed in a suspension of manganese dioxide.

Silvered asbestos was prepared according to the method of Fokin (27). Acid washed long-fiber asbestos was soaked in 15% silver nitrate solution and silver precipitated in the asbestos fibers by reduction with concentrated formic acid solution. Thorough washing with distilled water followed and the catalyst, silvery-grey in colour, was dried at 110°C.





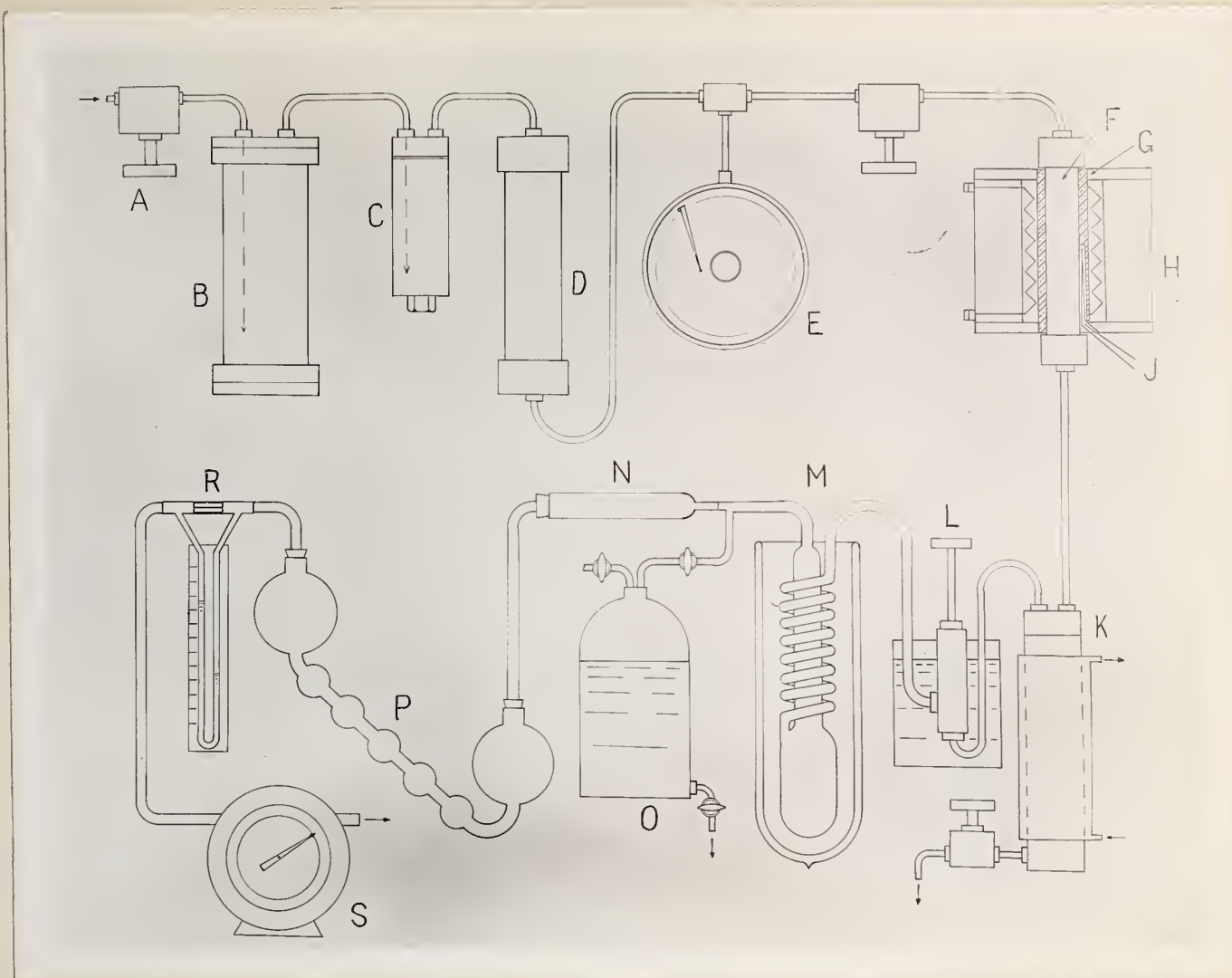


FIGURE 2.

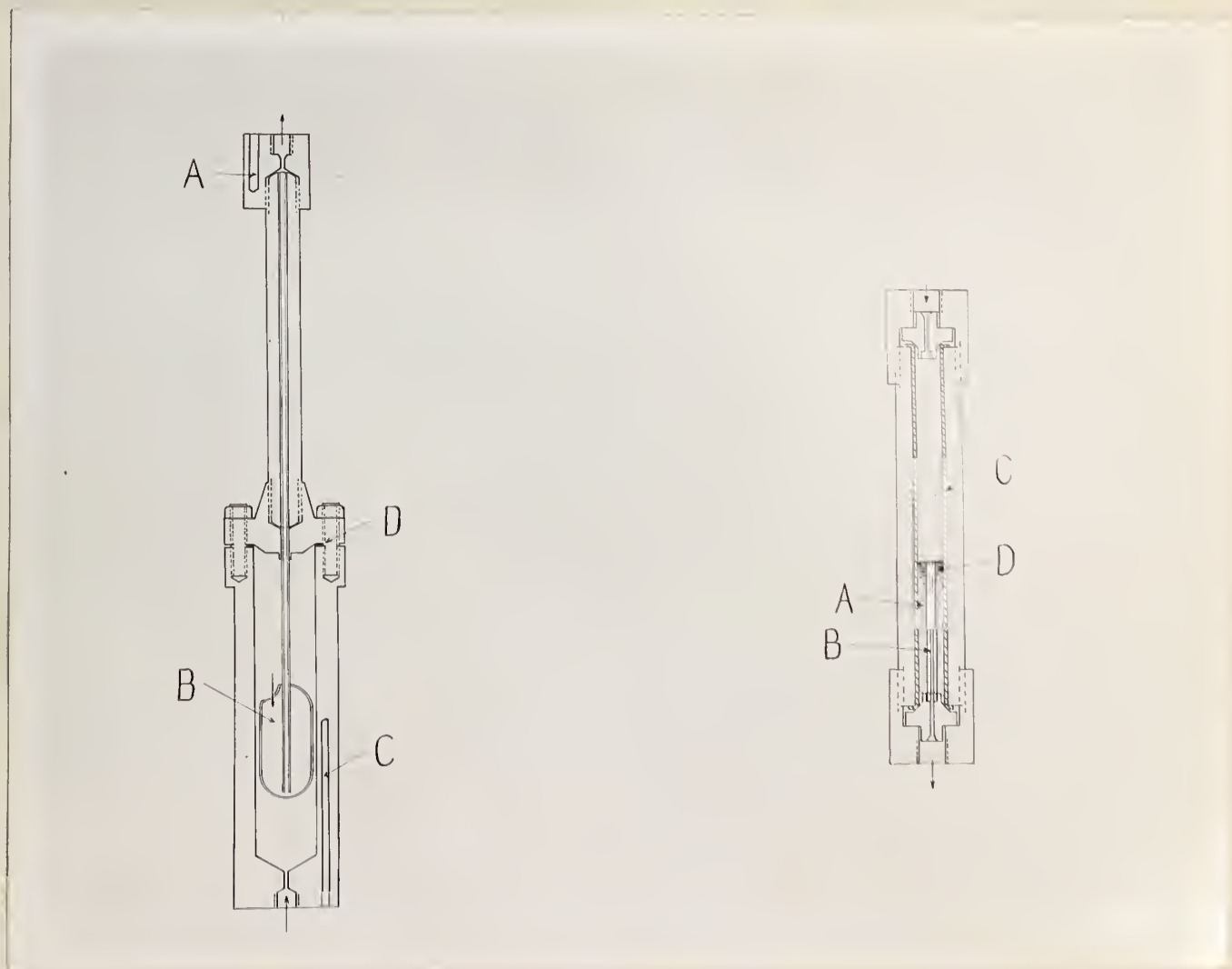


FIGURE 3.

FIGURE 4.





## Apparatus.

Figure 2 shows diagrammatically the apparatus employed in the high pressure oxidation of natural gas. The gas from storage enters the system through the valve A and is scrubbed under pressure in B with 98% sulfuric acid to remove the organic sulfur compounds used in odorizing the gas. Buffling of the gas flow was obtained by filling the scrubber with large pieces of broken glass. Any sulfur dioxide or sulfur trioxide produced in this step was removed by means of solid KOH in C, and a final purification was effected by means of activated charcoal in the absorber D. Besides ensuring removal of the sulfur compounds and water the charcoal reduces the ethane and propane content of the gas to low values.

A record of the gas pressure in an experiment was obtained by means of a recording pressure gauge E. The reaction chamber F which will be described in detail later was maintained at the desired temperature by means of the split multiple-unit electrical furnace H. Even distribution of temperature throughout the length of the autoclave was obtained by means of a split brass cylindrical jacket G placed between the reaction chamber F and the heating elements. The temperature was determined by means of a thermocouple, J, inserted





in a groove cut in the inner surface of the brass cylinder G, and exposed to the wall of the reaction chamber.

The gas mixture entered at the top of the reaction chamber and the products left at the bottom and were removed at the bottom, and were led directly to the bottom half of the pressure condenser K. The gas leaving the condenser was expanded to atmospheric pressure, through the heated expansion valve L. Further removal of oxygenated compounds from the gas was effected at atmospheric pressure by means of the ice-condenser M, the calcium chloride tube N and the Meyer scrubber P containing distilled water. The differential flow meter R indicated the rate of gas flow and the total volume of off-gas was recorded by the Sargent wet-test meter S containing mineral seal oil.

The high pressure steel connecting tubing, 1/16" x 1/4", valves and connections were generally of the type described by Ernst (12). Gas-tight gaskets on the purifiers and reaction vessels were of annealed copper except in the case of the bottom gasket in the sulfuric acid scrubber B, which was made of lead to withstand the corrosive action of the acid. The body and end-plates of the scrubbers B and C, were of a high nickel-chromium stainless steel, which was found to be unattacked by the acid.





Two different reaction chambers were used in the experiments. Their construction is shown in figures 3 and 4. For the first nineteen runs the reactions were carried out in the larger autoclave, figure 2, while the small autoclave, figure 3, was used for all succeeding runs. The body of the larger autoclave was constructed of a high nickel-chromium steel with a chamber 1 5/8" diameter by 11" long. The thermocouple for temperature control was located in the well shown at C. The catalyst was placed in the pyrex glass vessel B attached to the lower end of a glass tubing running right to the upper end of the column 12" long. The gas entered at the bottom of the reactor and had ample time to come up to temperature before entering the top of the catalyst chamber B. The central glass tube through which the products left the apparatus was sealed to the metal head A by means of deKhotinsky cement. This reactor was not found suitable for the investigation as it was necessary to maintain the head A cool enough that the cement seal would not melt, and consequently any liquid products would be condensed and returned to the autoclave.

The smaller reaction chamber shown in figure 4, and also in the flow diagram, figure 2, was much more satisfactory. High nichel chromium steel was used for





the body and ends. The copper lining C extended over the ends of the body as shown in the diagram and acted as a gasket. In order to support the catalyst at the centre of the chamber in close proximity to the thermocouple, and also to enable the rapid removal of products after the gas had passed over the catalyst, a piece of pyrex tubing B was inserted as indicated, and the space, A, between this tubing and the walls of the autoclave was packed with clear quartz sand of no catalytic effect. A packing of asbestos fiber at D served to keep the sand in place.

The pressure condenser K of phosphor bronze was cooled by tap-water circulated in the jacket as shown in fig.2. Due to the low space velocities of the gas at high pressure the removal of condensable liquid products in the pressure condenser was virtually complete. It was found necessary to chromium plate the inside surface of the pressure condenser to prevent solution of copper by the formic acid formed in the reactions.

The expansion valve L also of phosphor bronze was immersed in an oil-bath maintained at about  $110^{\circ}\text{C}$ . to counteract the adiabatic cooling on expansion of the gas which would cause freezing of the liquid products in the line.



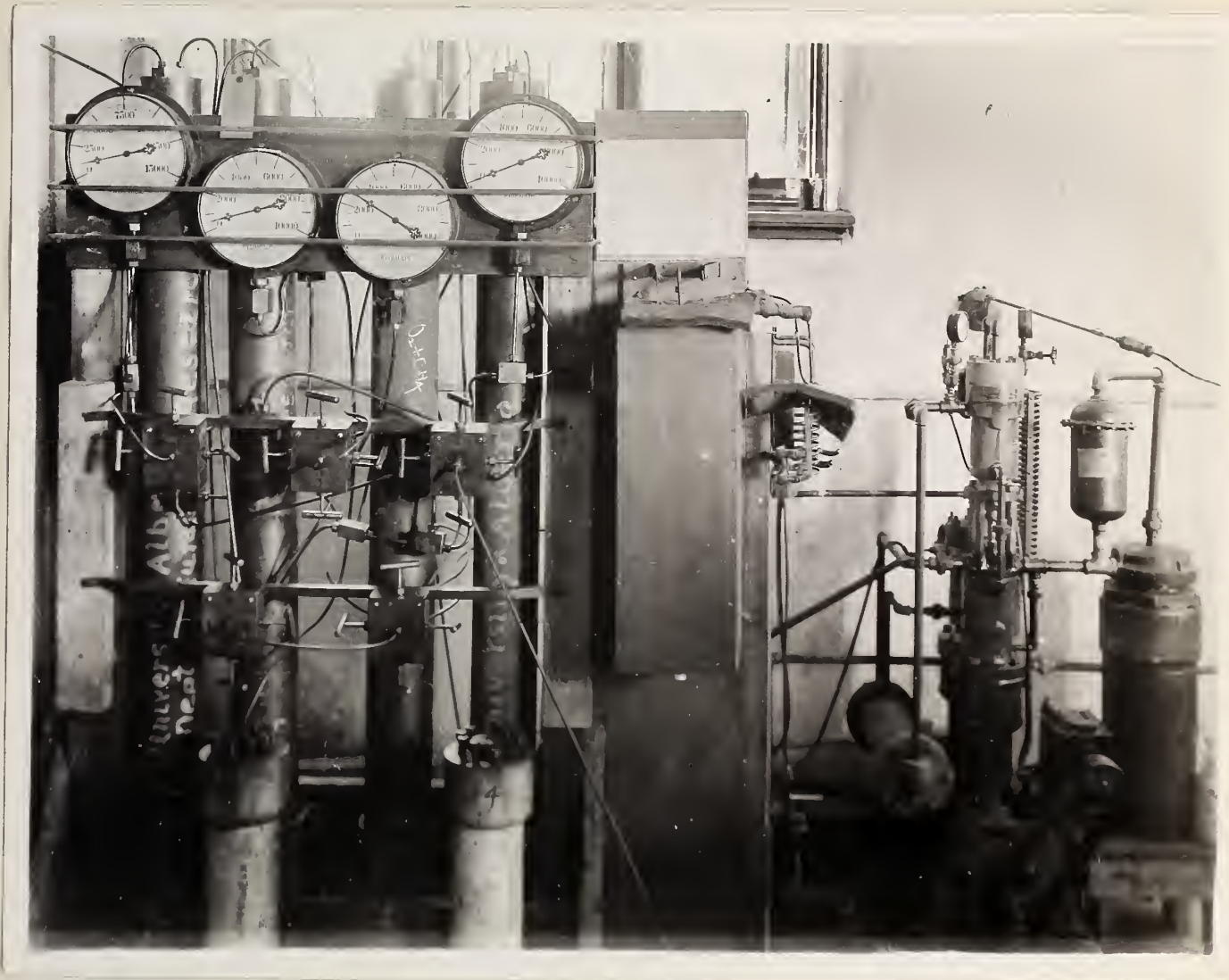


Fig. 1.

Compression and Storage System.







FIGURE 5.

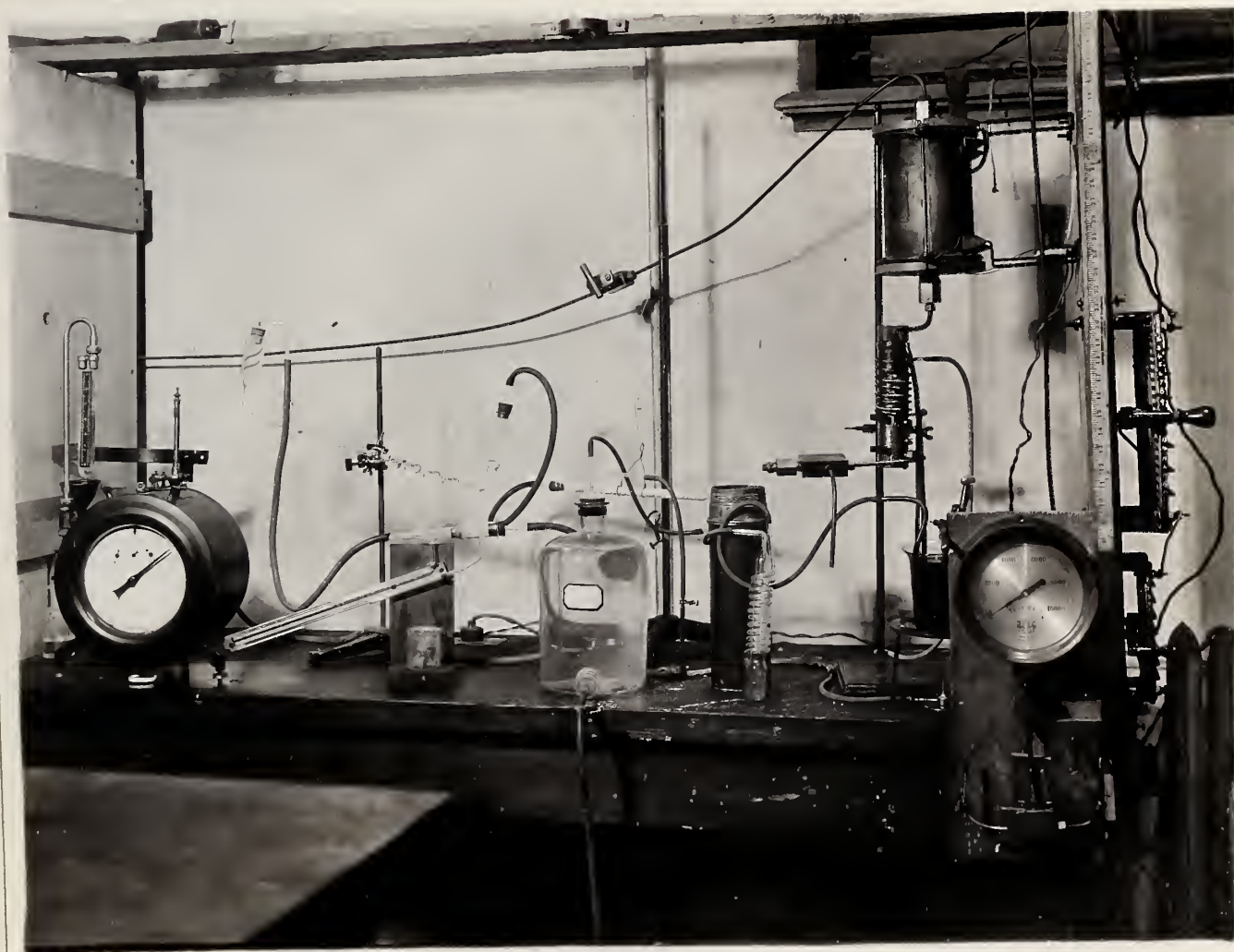


FIGURE 6.





The measuring instruments used may be briefly described. The recording pressure gauge, E, figure 2, was calibrated by comparison with a dead weight piston gauge calibrated at the National Physical Laboratory, England. The temperatures of the reaction chamber were recorded to  $\pm 1^{\circ}\text{C}$ . and controlled to  $\pm 5^{\circ}\text{C}$ . by a potentiometer type recorder controller actuating the necessary relays. Calibrated iron-constantin thermocouples were used. The replaceable capillary tube type flowmeter R, and test meter S, were calibrated by positive displacement methods.

Photographs of the equipment, figure 1, the compression and storage system; figure 5, the temperature controller, sulfuric acid scrubber, caustic scrubber, charcoal container and pressure recorder; and figure 6, the reaction, condensing and collecting system are shown. The furnace and enclosed reactor, with condenser below it are obvious. There follows from right to left the oil bath containing the expansion valve, the blow-off valve on the pressure condenser, the atmospheric condenser removed from the Dewar flask ice-bath behind it, the calcium chloride tube and the gas sampling bottle, the flowmeter with sloping pressure gauge, with the Meyer washing tube above it, and lastly the test meter. The test gauge in the lower right





hand corner in front of the expansion valve belongs to other equipment.

### Analytical Methods.

The liquid products of the reactions together with formaldehyde were condensed almost completely in the high pressure condenser. It was usual to find less than 0.5 gms. in the ice-cooled condenser and only a few tenths of a gram increase in weight in the calcium chloride tube. Traces of formaldehyde that escaped condensation in the condensing system were efficiently collected by the distilled water placed in the Meyer absorption tube at the end of the collecting train. At the conclusion of a run the contents of the high-pressure condenser were blown into the ice-cooled condenser, its increase in weight determined, and the whole transferred to a 100 ccm. volumetric flask. The contents of the Meyer tube were added to the volumetric flask and the volume made up to 100 ccm. with distilled water. Measured portions of this solution were taken in turn for the determination of alcohols, formaldehyde and formic acid. The total weight of products was taken as the weight of liquids recovered from the high pressure condenser in the ice-cooled condenser plus the small increase in weight of the calcium chloride tube.





The material collected in the calcium chloride tube was doubtless largely water and was considered all water in subsequent calculations of the amounts of the various products. The whole correction was at all times small and it was probable that the methyl alcohol portion was less than 0.5% of the total product. The weight of formaldehyde collected in the Meyer tube was neglected compared to the total weight of products, being less than the experimental error in view of the small total production of formaldehyde.

The off-gas from the apparatus was passed through an oil-filled wet-test meter for measurement. A continuous sample of the gas was taken over a 20% sodium sulfate solution containing 5% of sulfuric acid throughout the course of an experiment for analysis. All analyses were carried out in the Burrell improved type of Bureau of Mines apparatus. Carbon dioxide was determined in potassium hydroxide solution, olefines in fuming sulfuric acid, and oxygen in alkaline pyrogallate solution. Carbon monoxide and hydrogen were determined by combustion over copper oxide, and paraffin hydrocarbons by combustion with oxygen on platinum.





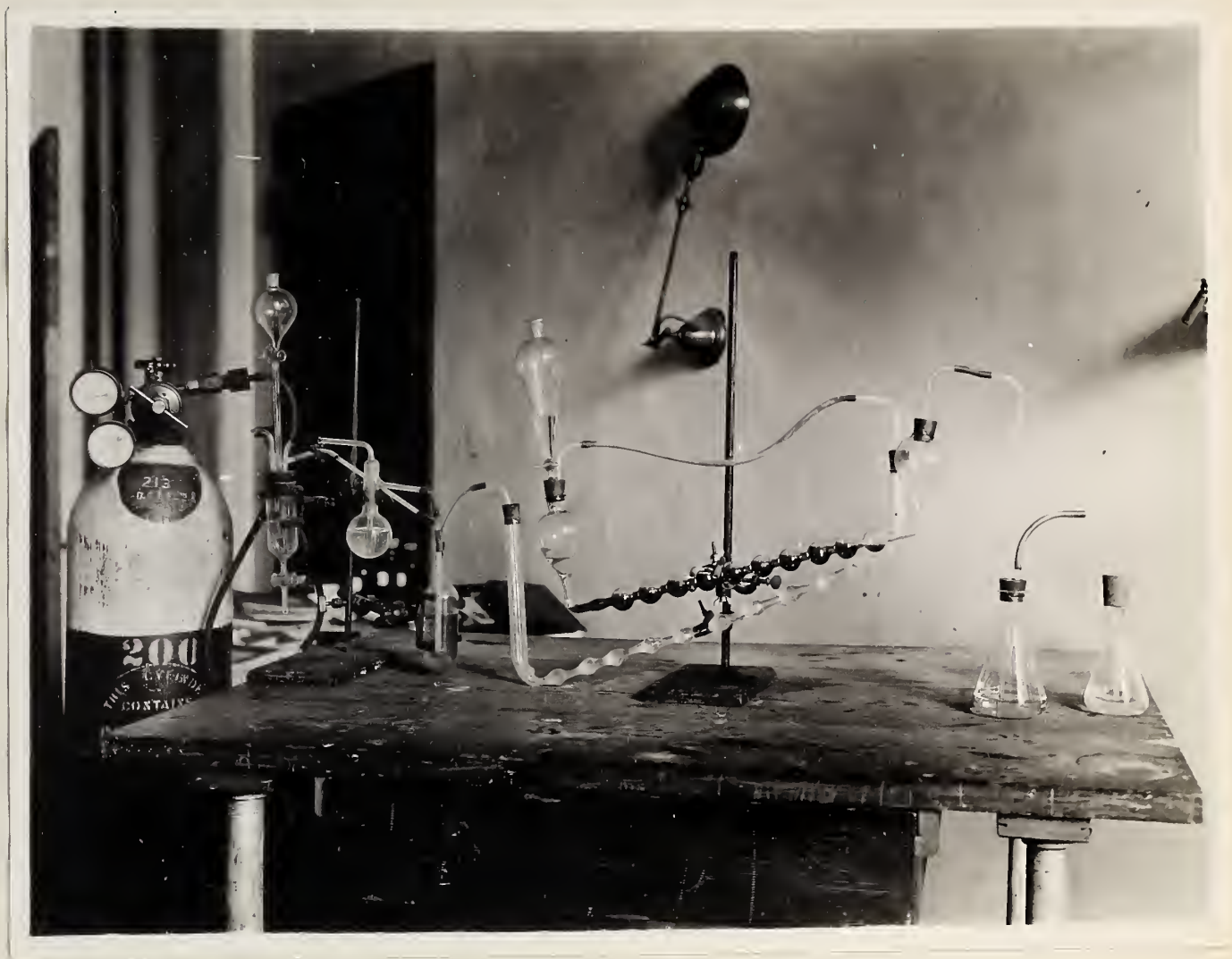


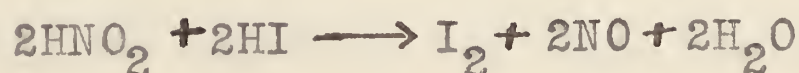
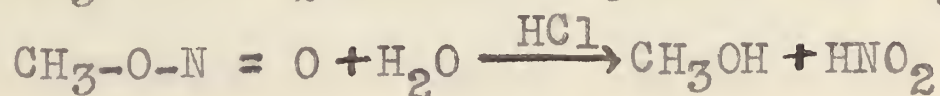
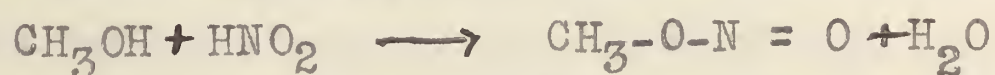
FIGURE 7.



### Methyl Alcohol Determination.

Many methods are described in the literature for the determination of methyl alcohol. Most of these are oxidation methods, but since the condensates contained other organic compounds which are readily oxidized these methods could not be employed with any degree of accuracy in the present work.

The method of Fischer and Schmidt (26) was adopted with slight modifications as being the most satisfactory. This method depends on the quantitative formation of methyl nitrite and its subsequent hydrolysis to methyl alcohol and nitrous acid by hydrochloric acid in the presence of potassium iodide. The iodine liberated by the nitrous acid is then titrated with standard sodium thiosulfate solution, one gram molecular weight of sodium thiosulfate being equivalent to one gram molecular weight of methyl alcohol according to the following reactions:-







The apparatus shown in Figure 7 consists of first, a decomposition vessel visible at the left end of the train. This is equipped with a gas inlet leading to the bottom, a dropping funnel, and a drain cock at the bottom. The decomposition vessel is followed by a gas washing bottle and a Meyer tube containing saturated solutions of sodium bicarbonate to remove higher oxides of nitrogen, and a second Meyer tube containing a solution of 4 gm. KI and 10 ccm. of concentrated hydrochloric acid in about 30 ccm. of water. This second Meyer tube is followed by a guard flask containing a solution of 1 gm. KI and a few drops of concentrated hydrochloric acid. The right hand Erlenmeyer flask prevents accidental access of air to the apparatus. The success of the method depends upon the careful and complete elimination of oxygen from the system.

In making a determination all the air in the apparatus is first displaced by nitrogen, from the cylinder shown on the extreme left of the figure, which gas was found to be more convenient to use than carbon dioxide, as proposed by Fischer and Schmidt. The potassium iodide solution may then be introduced through the dropping funnel shown. A definite volume of the alcohol solution is introduced into the reaction flask from its dropping funnel, together with 10 ccm. of





saturated sodium nitrite solution and 20 ccm. of 25% acetic acid solution. The methyl nitrite formed, which is a gas at ordinary temperatures, is almost completely removed from the reaction mixture in about one hour by the gas stream, but it is necessary to continue passing through nitrogen for another 45 minutes in order to remove all the nitric oxide before disconnecting the apparatus for titration.

Fischer and Schmidt have found that the results obtained by this method are precise in the presence of aldehydes, ketones, organic acids and ethers.

Certain identification of the alcohol present was obtained with samples separated and purified by fractionation which were identified as methyl alcohol by the 3-5 dinitrobenzoic acid ester derivative, M.P.  $106.8^{\circ}\text{C}$ . A mixed M.Pt. determination was also made using some of the ester prepared above together with pure methyl, 3,5-dinitrobenzoic acid ester. The M.Pt. of this mixture was also  $106.8^{\circ}\text{C}$ . The iodoform reaction showed the presence of ethyl alcohol in small amounts as would be expected from the presence of ethane in the original gas used.





### Determination of Formaldehyde.

Formaldehyde was determined by Romijn's cyanide method (19) which is specific for this compound. The use of 0.1 N standard solutions was found to be quite in keeping with amount of aldehyde to be determined when 10 ccm. samples of the diluted condensate were used. However, the procedure outlined in Allen's organic analysis (1) was modified somewhat as mentioned below in order to reduce the experimental error.

A 10 ccm. aliquot portion of the diluted condensate is treated with an excess of 0.1 N KCN solution. The soluble addition product of formaldehyde and KCN forms immediately, one molecule of formaldehyde combining with one of KCN. The excess KCN is determined by Volhard's method as follows: After the sample has been treated with an excess of KCN solution it is washed into a 100 ccm. volumetric flask containing exactly 10 ccm. of 0.1N silver nitrate solution and a few drops of dilute nitric acid. The excess KCN precipitates as AgCN, and the volume is made up to 100 cc. The solution is then filtered through a dry filter into a dry flask, and the excess silver nitrate in a 50 ccm. aliquot portion of the filtrate is determined by titration with 0.1N KCNS solution using ferric alum indicator.





The use of a 50 ccm. aliquot portion of the filtrate involves a smaller experimental error than the use of a 10 ccm. portion as recommended by Allen. From the above data the amount of formaldehyde present may be calculated.

Results by this method are accurate even in the presence of acetaldehyde which forms an addition compound very slowly with KCN.

#### Formic Acid.

Formic acid was determined by warming a 10 ccm. sample of the condensate to expel carbon dioxide, cooling, and titrating with 0.05 N NaOH. During some of the earlier runs, before the high-pressure condenser had been plated with chromium, the formic acid attacked the bronze body of the condenser and appeared as copper formate. The formic acid in these solutions was determined by adding an excess of 0.05N NaOH solution, rapidly filtering off the precipitated copper hydroxide by suction, and back titrating the filtrate with 0.05N sulfuric acid.

The pipettes and burettes used in all the above determinations were calibrated, and the solutions which were likely to change in concentration, such as sodium thiosulfate and potassium cyanide, were checked from time to time.





Distillation.

A Cooper and Fasce microfractionating column (9) was used for separating and purifying the alcohols by distillation for subsequent identification as the 3,5-dinitrobenzoic acid ester derivatives. This apparatus was of small size and equipped with a 12 inch vacuum jacketed point and bulb column and a controlled reflux condenser. It gave good results with samples as small as 10 ccm.



[illegible]





TABLE II.

Experiment No.	12	13	14	15	16	17	18	19
Catalyst No.	III	III	III	None	None	None	None	None
Temperature °C.	230	350	400	250	300	375	425	275
Pressure atmospheres	142.5	142.5	140	123	123	122	122	98.0
Flow, litres/ min.Exit Gas	.57	.77	.78	.80	.80	.80	.80	.80
Gas Analysis								
CO <sub>2</sub> %	0.0	0.9	1.2	0.1	0.4	1.2	1.5	0.1
Unsat.	0.0	0.0	0.2	0.0	0.1	0.1	0.2	0.1
O <sub>2</sub>	6.1	2.4	0.1	6.9	4.4	1.4	0.1	7.1
H <sub>2</sub>	0.0	0.8	1.7	0.1	0.8	1.3	2.1	0.3
CO	0.6	1.9	3.7	0.0	0.9	2.7	3.6	0.0
CH <sub>4</sub>	-	-	82.7	85.2	86.8	85.0	87.1	86.4
C <sub>2</sub> H <sub>6</sub>	-	-	0.5	1.4	0.5	0.5	0.0	0.5
N <sub>2</sub>	-	-	9.8	6.3	6.1	7.8	5.4	5.5
Condensate gms.	0.0	0.0	0.0			5.0		0.0
Methyl Alcohol gms.	0.0	0.0	0.0			0.4		0.0





TABLE III.

Experiment No.	20	21	22	23a	23b	23c	24	25	26	27	28	29	30	31	33	34	36	37	39	40	43	45	46
Catalyst No.	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	IV	Cu	VI	VI	VI	VI	V	VII	VII
Temperature °C.	250	338	400	325	335	340	325	275	325	325	350	350	350	350	350	350	266	281	311	325	241	310	312
Pressure atms.	150	143	141.5	131.8	124	161.5	182.8	172.5	160.5	118.5	116.5	109.3	96.0	214	162	117	203	190	157	145	91.5	173	153
Exit Gas Flow litres/min.	-	-	-	1.0	1.0	1.0	0.8	0.9	0.58	0.9	0.9	2.0	2.0	2.3	1.3	0.9	2.0	2.0	1.9	1.9	2.0	2.0	3.82
Total Gas Passed cu.ft.	-	8.39	-	-	8.29	-	6.328	4.792	5.05	9.525	7.622	9.493	8.441	9.000	8.268	6.576	8.600	9.015	8.747	6.278	7.400	7.667	11.868
Inlet Gas; %O <sub>2</sub>	7.5	7.5	7.5	7.5	7.5	7.5	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Gas Analysis																							
CO <sub>2</sub> %	0.0	2.4	2.8	0.8	2.45	2.6	2.25	0.7	2.9	1.4	2.55	2.0	2.45	1.2	1.5	2.25	1.1	0.9	4.25	1.6	0.0	1.4	1.65
Unsat.	0.2	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00
O <sub>2</sub>	6.9	0.3	0.0	5.8	0.35	0.1	1.4	6.65	1.7	3.35	0.45	0.35	0.1	0.6	0.0	0.6	4.6	4.8	0.1	0.2	6.55	0.1	0.95
H <sub>2</sub>	0.5	0.5	0.3	0.0	0.35	0.2	0.35	0.95	0.25	0.25	0.45	0.45	0.35	0.2	1.05	0.35	0.3	0.3	2.0	0.6	0.3	0.35	0.5
CO	0.1	1.0	1.9	0.0	1.4	0.95	0.6	0.0	0.75	0.7	1.4	1.9	1.95	1.8	3.0	1.5	0.2	0.0	0.8	3.25	0.2	1.55	2.25
CH <sub>4</sub>	-	-	-	87.5	84.8	90.3	84.8	84.9	94.3	86.8	89.5	88.1	86.8	-	-	-	-	-	82.7	-	-	89.10	90.1
C <sub>2</sub> H <sub>6</sub>	-	-	-	0.5	0.0	0.0	2.4	1.8	0.0	0.0	0.0	0.45	1.4	-	-	-	-	-	1.2	-	-	0.0	0.0
H <sub>2</sub>	-	-	-	5.3	5.65	5.85	8.1	5.0	5.7	7.4	5.65	6.75	6.95	-	-	-	-	-	8.95	-	-	7.5	4.55
Ratio CO <sub>2</sub> /CO	-	-	-	0.0	0.570	0.365	0.267	0.0	.258	0.500	.548	0.95	0.795	1.50	2.0	.587	-	-	-	-	-	-	-
Condensate gms. <sup>a</sup>	-	4.8	-	-	12.1	-	14.2	0.0	14.1	7.6	18.00	19.32	16.05	19.32	18.55	19.39	3.48	2.16	13.49	10.5	0.4	19.72	15.4
CH <sub>2</sub> OH gms.	-	1.4	-	-	-	-	5.5	0.0	4.38	2.76	5.94	7.09	6.52	8.12	6.24	6.56	.0799	-	2.25	3.34	-	4.82	3.05
HCHO gms.	-	-	-	-	-	.1163	0.0	0.0	.1600	.0991	.226	.182	.352	.276	.361	.400	-	-	.1527	.0689	-	.263	.222
HCOOH gms.	-	-	-	-	-	-	0.0	0.0	-	-	.1000	.0762	.0275	2.13	.0768	.0748	-	-	.0364	.0373	-	.124	.0921
H <sub>2</sub> O gms.	-	3.4	-	-	-	-	5.3	0.0	4.2	4.8	11.73	11.97	9.15	10.53	6.68	11.33	3.4	-	11.15	7.05	-	14.52	12.04
% CH <sub>2</sub> OH in Condensate	-	29.2	-	-	-	-	38.7	0.0	31.2	36.2	33.0	36.7	40.6	42.0	33.8	33.8	2.28	-	16.7	31.7	-	24.4	19.8
Carbon Oxidized gms.	-	-	-	-	-	5.77	-	-	6.49	3.84	7.40	7.78	8.24	9.39	8.295	7.717	-	-	7.344	7.52	-	5.75	7.39
Carbon Oxidized to oxygenated compounds	-	-	-	-	-	2.12	-	-	1.70	1.08	2.35	2.75	2.59	5.07	2.505	2.867	-	-	.874	1.289	-	1.953	2.257
Yields as % of Carbon turned:-																							
CH <sub>2</sub> OH	-	-	-	-	-	-	35.9	-	25.3	27.1	30.15	34.2	29.7	32.4	28.2	31.8	-	-	11.5	16.6	-	31.5	15.41
HCHO	-	-	-	-	-	-	0.8	-	0.98	1.04	1.22	.934	1.71	1.17	1.75	2.07	-	-	.287	.365	-	1.74	1.20
HCOOH	-	-	-	-	-	-	-	-	-	-	.35	.255	0.09	20.4	0.24	3.19	-	-	.150	.146	-	.64	.374
Total	-	-	-	-	-	36.7	-	-	26.2	28.1	31.7	35.3	31.4	54.0	30.2	37.15	-	-	11.94	17.11	-	33.88	16.98

<sup>a</sup> The weight of products is expressed in gms. per 10 cu.ft. of gas as measured.

## Catalysts:

I - BaO<sub>2</sub> 1st PreparationII - BaO<sub>2</sub> 2nd Preparation.III - V<sub>2</sub>O<sub>5</sub>

IV - Blue Tungsten Oxide.

V - Hopealite I

VI - Hopealite II

VII - Silvered Asbestos.



## EXPERIMENTAL RESULTS.

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The experimental results may be classified according to the gas used and the autoclave used into three groups. The first of these, including experiments 1 to 11 given in Table I, was carried out on natural gas without any oxygen. The large reactor, described previously, was used. The second group, Experiments 12 to 19, shown in Table II were carried out on natural gas-oxygen mixtures in the same reactor, and the third group, experiments 20 to 46, Table III, were carried out on natural gas-oxygen mixtures in the small copper lined reactor. It should be emphasized at this point, that while in these tables a catalyst is listed for each experiment, either iron or copper was present also. In using the large autoclave, the steel walls would always be exerting their catalytic effect in addition to that of any added catalyst, and the same is true for copper in the experiments given in Table III. In the tables, only added catalysts are given numbers; when only the iron or copper walls were catalysts, the catalyst is listed as Fe or Cu.

The purpose in carrying out the experiments with natural gas alone was to investigate oxides which might be capable of oxidizing the gas, the oxides being reduced in the process to a lower oxide or the metal.





These substances were the higher oxides of metals having more than one possible valence, the same oxides being used later as catalysts with mixtures of natural gas with oxygen. Any oxidation of the gas would be shown by the appearance of carbon monoxide or carbon dioxide in the off-gas, and also by the possible formation of a condensate consisting of water and perhaps oxygenated organic compounds such as methyl alcohol, formaldehyde, and formic acid. In none of these experiments was oxidation detected by analysis of the products, and yet, in some cases the oxide was apparently reduced. The reduction of the oxide may have taken over a short period of time and to a limited extent, also under such conditions, the method of sampling used might fail to give a representative sample. The inability of the oxides used to oxidize methane was not entirely unexpected in view of the relatively great stability of methane to any but the most active catalysts below  $600^{\circ}$  to  $700^{\circ}\text{C}$ . The Hopcalite catalysts were not used in this series of experiments but it is probable, in view of their great activity on methane-oxygen mixtures, that they might have been effective. However, as shown in this laboratory and elsewhere (14) these catalysts are extraordinarily reactive, and once reduced, lose their activity and cannot be regenerated.





The results of the first eleven experiments, using natural gas without oxygen, are therefore of little interest to the present work and may be dismissed without further discussion.

Experiment No. 12 and all those succeeding were made with oxygen-natural gas mixtures, the first eight of these being made in the large reactor. Small amounts of liquid products were obtained in the first eight, sometimes containing methyl alcohol as shown by distillation in the micor-fractionating column. However, on opening the autoclave at the conclusion of these experiments comparatively large amounts of liquid, which had been condensed in the column, were found and corrosion was evident. In view of this serious disadvantage of the larger autoclave its use was discontinued. The results of the experiments are of value, however, as a study of the catalyst activity on the basis of oxygen consumed. The presence of  $H_2$  and CO in the off-gas indicate fairly conclusively that methanal and its oxidation products were formed, but quantitative work was not possible.

The final series of experiments from No. 20 to No. 46 were done in the small copper-lined reactor, which was found to be very satisfactory for the purpose.



The experience gained in the first two series of runs led to much more satisfactory technique. It was found that the composition of the gas varied somewhat throughout the course of an experiment, and in order to obtain representative samples of the off-gas, an average was taken in an aspirator bottle.

Pressures were noted as recorded, corrected and an average taken for the run. Usually a drop in pressure of about 100 to 200 lbs. per sq.in. occurred. The rate of gas flow was controlled by observing a capillary flowmeter, which served only as a rough estimate of the rate of flow over the catalyst. However, by this means a constant rate was maintained and comparative results were obtainable.

The temperature of the autoclave was controlled by three rheostats in series. When oxidation of the gas was taking place, it was noted that considerably less current was necessary to maintain the temperature at that desired, due to the heat liberated in the reaction. Sudden temperature rises of the order of  $15^{\circ}\text{C}$ . were frequently noted on commencing gas flow.

There was no means available for direct measurement of the quantity of gas mixture entering the reactor at the pressure of the system. An indirect





calculation was possible, however, from the total weight of gaseous and liquid product, but the information obtained would be of such small significance as to make the laborious calculation necessary hardly worth while. The important quantity desired was the efficiency of the process in terms of the fraction of all the methane oxidized that goes to useful products. Calculations of the percentage of various oxygenated compounds formed on the basis of total carbon oxidized were made from the composition and volume of the off-gas together with the weights of methyl alcohol, formaldehyde, and formic acid obtained. The value is of course an indirect one but there is no reason to suspect its validity beyond the limits of the experimental errors in the analytical methods.

The results of Experiment 30 may be taken as typical and the necessary calculations illustrated in order to explain most simply the method. The same type of calculation as shown below was of course necessary for each experiment.

Experiment 30.

Data.

% CO<sub>2</sub> in off-gas = 2.45

% CO in off-gas = 1.95

Barometric Pressure (Corr.) = 701.3 mm.





Temperature of gas-meter =  $23^{\circ}$  C.

$\text{CH}_3\text{OH}$  per 10 cu.ft. of off-gas = 6.52 gms.

$\text{HCHO}$  per 10 cu.ft. of off-gas = .352 gms.

$\text{HCOOH}$  per 10 cu.ft. of off-gas = .0275 gms.

Calculation.

$$\text{Gm.mals. of off-gas} = \frac{283.2}{22.412} \times \frac{701.3}{760} \times \frac{273}{296} = 10.75$$

$$\text{Gm. atoms. of C in } \text{CO}_2 = \frac{2.45}{100} \times 10.75 = .264$$

$$\text{Gm. atoms. of C in CO} = \frac{1.95}{100} \times 10.75 = .210$$

$$\text{Total} = .474$$

$$\text{Gms. C in } \text{CO}_2 \quad \text{CO} = .474 \times 12 = 5.69$$

$$\text{Gms. C in } \text{CH}_3\text{OH} = 6.52 \times \frac{12}{32} = 2.44$$

$$\text{Gms. C in } \text{HCHO} = .352 \times \frac{12}{30} = .141$$

$$\text{Gms. C in } \text{HCOOH} = .0275 \times \frac{12}{46} = .00717$$

Total wt. of carbon oxidized 8.278

Total wt. of C converted to useful  
oxygenated compounds = 2.588

Fraction of carbon oxidized that goes to useful  
oxygenated compounds as percent by weight:

to $\text{CH}_3\text{OH}$	29.7 %
to $\text{HCHO}$	1.71 %
to $\text{HCOOH}$	0.09 %
Total	31.5 %

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Discussion.

From a study of the oxygen consumption as shown in Tables I, II and III and in the numerous exploratory experiments searching for the active region, which are not tabled, the relative activity as measured by the temperature of initial oxidation and the temperature at which oxidation is complete, and also the temperature at which the catalyst acquires permanent activity may be deduced. The resulting conclusions are given in Table IV below.

TABLE IV.

Catalyst	Fe	V <sub>2</sub> O <sub>5</sub>	Cu	W <sub>2</sub> O <sub>3</sub>	Ag	HI	HII
Temp.of Initial Activity 0°C.	375	350	325	325	300	125,165	175,280
Temp.of Good permanent activity	425	400	350	350	310		310

In the case of the Hopcalite catalyst an explanation for the two figures for initial activity is due. The same samples of catalyst was used throughout in each case, and the figures refer to the initial behavior of fresh catalyst. The first figure gives the temperature





of initial activity, but in both cases reaction ceased in a short time to reappear only on raising the temperature to the second figure given. The activity of the catalyst disappeared again after a short time and oxidation of the methane was only found possible at the higher temperature given in the lower row. At this temperature of  $310^{\circ}\text{C}$ . a state of permanent activity was reached. This behavior was not found to be reversible as the catalyst showed no activity at lower temperatures once it had been heated to  $300^{\circ}\text{C}$ . The ability of Hopcalite catalysts to oxidize methane to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  below  $100^{\circ}\text{C}$ . at atmospheric pressure illustrates its extreme activity and at the same time, sensitivity to severe treatment. It is probable that a rapid reaction occurred at the lower temperature, and that the catalyst was momentarily at a much higher temperature than that indicated by the thermocouple. The Hopcalite on removal from the reactor had obviously undergone serious alteration - shrinkage and color change typical of sintering. A loss of activity, due to change in surface structure and reduction, would be a natural consequence. The reason for the existence of two regions of temporary activity is not clear. It may be suggested, however, that it is due to the binary nature of the Hopcalite catalysts; the  $\text{H}_2\text{O}_2$





would be deactionated first at the lower temperature because of its highly active nature and the CuO at the second and higher temperature. The promoter action of cobalt and silver oxides was made evident in the case of the Hopcalite I by the lower temperature of initial activity.

From an inspection of Table IV, it is evident that iron and Vanadium pentoxide are not suitable catalysts at the temperatures for reaction, the reaction goes largely to completion forming carbon oxides,  $H_2$  and water. Silver and used Hopcalite appear to be equal in activity and the choice of the best one will depend upon their other qualities governing the efficiency of the process. While copper and blue tungsten oxide require higher temperatures, i.e., are less active, they must also be considered in the light of their performance in the production of useful products before a final decision as to the most promising catalyst can be made. Finally when comparing these catalysts the presence of steel walls in the experiments with  $V_2O_5$  and the presence of copper walls with the last four catalysts listed must be taken into account. Fortunately, the effect of adding a catalyst is evident in every case, but one by the development of activity at a lower temperature. The presence of  $W_2O_3$  in the small auto-





clave did not alter the temperature of activity in the slightest and it might be said that  $W_2O_3$  had no catalytic effect. Consideration of the products of the reaction in the presence and absence of  $W_2O_3$  is necessary to determine the catalytic effect, if any.

Of the catalysts investigated copper, as represented by the copper lining of the small autoclave, was found to be the most efficient with regard to the production of intermediate oxidation products of methane. Very little, if any, variation in its activity after repeated use was noted. The optimum temperature of operation was in the neighborhood of  $350^{\circ}C$ . Decreased yields of methyl alcohol were obtained at other temperatures.

Experiments at various temperatures, pressures, and rates of flow were made with the purpose of determining the effect of these variables on the nature of the products obtained. A comparison of run 29 with run 31, which were made at the same temperature and approximately the same gas rate, indicates a large increase with increased pressure in the percentages of carbon burned surviving as intermediate oxidation products. There is a very marked increase in the yields of both the methyl alcohol and the formic acid,





accompanied by a slight increase in the formaldehyde. The increase in pressure is also accompanied by a decrease in the production of carbon dioxide and carbon monoxide. This is to be expected from volume relationships of the reactions occurring in the combustion according to the hydroxylation theory of combustion of hydrocarbons.

The effect of temperature may be noted by a comparison of the data for runs 27 and 28. The gas rate was 0.9 litres per minute and the pressures were comparable (116.5 and 118.5 atmospheres). However, the temperature in run 27 was 325°C, whereas, that of run 28 was 350°C. The total yield of condensate, and yields of the respective oxygenated compounds is approximately doubled by a 25 degree rise in temperature. The explanation lies in the fact that all the available oxygen was not utilized in run 27.

The rate of flow was not found to have such a marked effect as had the temperature and pressure. Runs 28 and 29 are comparable with regard to temperature and pressure, but the flow in Experiment 29 is slightly more than double that of Experiment 28. A definite increase in alcohol production is noted, accompanied by a slight decrease in the formic acid and formaldehyde. Since methyl alcohol is the first product





in the course of the oxidation, it is probable from these observations that a greater proportion of the methyl alcohol was removed from the reactor before further oxidation to formadehyde, formic acid, carbon dioxide and water. There is a limit to the rate of flow, however, as it might be increased to the point at which the amount of oxygen utilized would drop markedly. Indications of this are shown in Experiments 45 and 46 with silver, the oxygen survival increasing with flow rate. It may be predicted that the effect of changing the rate of flow would be small unless very large changes were made. The time that the gas was in the autoclave was relatively large in all experiments.

The results discussed above regarding the effect of changing the variables were all observed with copper as a catalyst, in the small autoclave. When the effects of these variables had been established, various other catalysts were investigated with a view to finding one which would materially lower the optimum temperature of operation.

The procedure in investigating these catalysts was first, to make short preliminary experiments to determine the temperatures of initial activity and optimum activity as indicated by the oxygen content of





the off-gas. The temperature was increased in steps and sufficient gas passed to flush out the pressure condenser before taking samples for analysis. When the gas analysis showed practically complete utilization of the oxygen, a run was made at that temperature and a high pressure, usually at a rate of 2.0 litres per minute of off-gas.

The Hopcalite catalysts gave very low yields of oxygenated compounds at the lowest temperature of complete utilization of oxygen. It had been hoped in the case of the Hopcalites that under the high oxygen pressure they would not be reduced, but would act rather as oxygen carriers. Reduction took place, however, and these catalysts were of no use at low temperatures. The Hopcalite catalysts showed excellent activity measured by oxygen survival at 300-310°C. which is some 40° to 50° below the optimum temperature for copper. However, the results expressed as efficiency of combustion were disappointing in that the yields of liquid products were very low in comparison with those obtained with copper as a catalyst.

Blue tungsten oxide (Run 33) was not found to lower the temperature of reaction below that for copper. But a definite effect may be attributed to





the tungsten oxide from an examination of the reaction products. At the optimum temperature of reaction,  $350^{\circ}\text{C}$ , the yields of useful products were very considerably lower than those obtained at  $350^{\circ}\text{C}$  with copper alone as a catalyst. This would indicate that oxidation was carried too far, a considerable amount of the intermediate products being further oxidized to  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The catalyst was obviously more active than copper in promoting these secondary oxidations.

The silvered asbestos catalyst showed considerable promise in that it promoted reaction in the region  $300^{\circ}$ - $310^{\circ}\text{C}$ . This is only to be expected as silver, or its oxide, is a well known oxidation catalyst. Examination of the products of the reaction confirmed the favourable impression made by the preliminary experiments, since yields of useful products were comparable with those obtained over copper. The extent of oxidation was slightly greater and the yields as a consequence smaller. However, the catalyst used was one of the most active forms of silver possible, and further, the supporting material not of the best type. It is believed that catalysts in the form of silver or a silver-plated base metal, such as copper, would prove to be more satisfactory in minimizing local over-





heating because of their better heat conductivity. Asbestos has very poor heat transfer properties and it is highly probable that the actual reaction temperature at the silver particles was higher than that recorded. Such a state of affairs would account for the greater degree of oxidation apparent in the results as compared to those obtained with copper. The silver catalyst differed in two other respects from the copper catalyst. First, the reactions on the surface were different in that the copper showed distinct evidence of oxidation and roughening of the surface, whereas, the silver was reduced more completely, as judged by colour, to the metallic form. Nothing could be concluded as to any physical changes in the silver because of its preparation on asbestos. Secondly, the presence of considerable methyl formate was evident in the off-gas. Methyl formate was always present in previous experiments, but only in relatively small amounts. Its formation would be suspected but only in small amounts on all but the tungsten oxide catalysts. However, it was not particularly evident except with the silver catalyst, 0.37 gms. being formed in experiment 45 and approximately 0.78 gms. in experiment 46, per 10 cu.ft. of off-gas. Silver has not been considered





a vapour phase esterification catalyst elsewhere, and it is quite possible that it was not acting as such here. It is rather more probable that the asbestos support promoted the esterification found. In this connection it should be pointed out that, whatever the cause, the catalytic action was slight since only a moderately good catalyst would remove all the formic acid in the presence of an excess of methyl alcohol such as obtains in these experiments.

From the behaviour of the Hopcalite catalysts and Vanadium pentoxide it is apparent that the higher oxides of metals or mixtures of these are not likely to prove suitable catalysts for the oxidation of methane. First, since they are poor conductors of heat it is probable that the heat liberated by the reactions on their surface raises the temperature to the point at which the oxides become sintered with consequent loss of activity. Secondly, at the temperatures necessary for reactions under pressure on such deactivated catalysts, the reaction cannot be controlled and proceeds to the secondary and final stages of oxidation. These oxides are inferior to tungsten oxide for the reactions desired which in turn was inferior to copper or silver. While it was expected that at high pressures in conjunction with





low temperatures and oxidation catalysts such as iron, vanadium or manganese oxides, the formation of meth-<sup>o</sup>anal would be promoted, the conclusion cannot be avoided that such is not the case. Rather, it can be said that, at moderate or low temperatures such as were used here the effect of pressure is to promote complete oxidation, the same as occurs at high temperatures at atmospheric pressure on such catalysts.





## Conclusions.

The use of catalysts in the direct oxidation of methane under pressure is promising in that the temperature of operation is reduced considerably below that (17) necessary with plain steel walls. In addition the yields are increased.

Metallic catalysts of the usual active type as typified by silver and copper are indicated. They are robust and efficient. They should be in massive form or carried on a support possessing excellent heat conducting properties.

Increased pressures are highly beneficial and not less than 200 atmospheres would appear to be desirable. The temperature of operation may be from 300-350°C.

Oxides of polyvalent metals such as Vanadium and Tungsten, which are typical high temperature oxidation catalysts, are not suitable. The same is true of the highly active low temperature oxidation catalysts such as the Hopcalite class.

Space velocities of the order of 5000 or more are possible over the metallic catalysts above without interfering with the yield which points to



commercial possibilities in the process. This space velocity figure refers to the gas volume, about 22.5% of the total, susceptible of reaction.

Yields as high as 37 % of the methane burnt as methanol, formaldehyde and formic acid are possible. If this total yield, 90% may be methanol. The aqueous condensate obtained contains methanol in concentration as high as 42%. These yields are higher than those found by Newitt and Haffner (17) in the absence of catalysts. Traces of ethane were present in the gas used and their presence results in the formation of ethanol as shown by a qualitative test on the condensate. This is only to be expected in the light of the work of Newitt and Haffner on ethane and suggests the examination of pure ethane in similar experiments.

Finally, there is no reason to believe that higher yields of useful products and a higher proportion of methanal cannot be obtained as the result of further investigations. These experiments would follow three main lines. The investigation of other metals in massive form, either singly or as couples, is obviously necessary. The use of higher concentrations of oxygen in the gas mixture needs examination





in view of the possibility of higher conversions and greater through put of material. Lastly the recirculation of the off-gas with addition of fresh oxygen should be investigated. This last proposal has attractive features in view of the possibility of the carbon oxides and Hydrogen in the off-gas suppressing, in part at least, the formation of such undesirable substances. The result would be a higher conversion to useful products, economy of gas and a greater through put.





# ACKNOWLEDGEMENT.

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The writer wishes to express his sincere thanks to Dr. E.H. Boomer, who directed this research and whose helpful advice, kindly criticism and generous assistance has enabled this work to be completed.

Also to acknowledge the use of the high-pressure equipment placed at his disposal by the Research Council of Alberta ~~and the National Research Council of Alberta~~ and the National Research Council of Canada.

The assistance of all those who in any way have aided in the preparation of this report is deeply appreciated.



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